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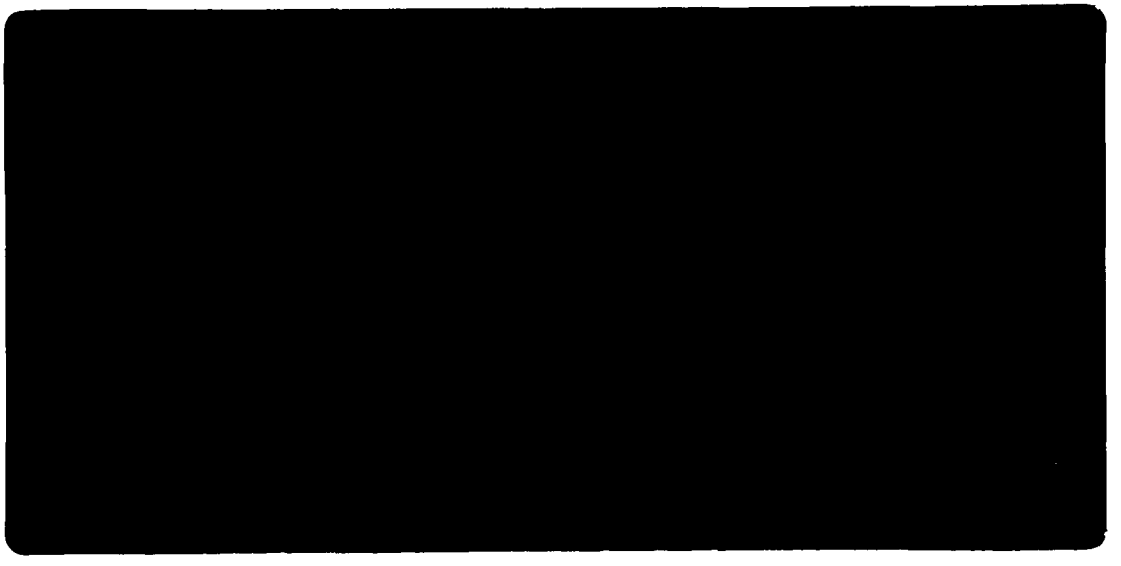

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PROCESS SIMULATION OF CHLORINE DIOXIDE SUBSTITUTION

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ABSTRACT

Modular Analysis of Pulp and Paper Systems (MAPPS) was used to simulate the chlorine dioxide substitution of chlorine in the kraft pulp bleaching sequence. The work, contained in the CSUBD process module, assumed that chlorine dioxide substitution behaved as a competing/parallel reaction sequence. Kinetic parameters and reaction pH were varied as the level of chlorine dioxide substitution was increased. Variation of pH was based on experimental data. Kinetic parameter variables were altered in accordance with literature data on the relative consumption of chlorine and chlorine dioxide during chlorine dioxide substitution. A novel solution technique, the Reverse-Variable Approach, was employed to solve the stiff ordinary differential equations that describe the chlorine and chlorine dioxide kinetic equations.

Simulation case studies were conducted in order to determine the validity of the assumed kinetics and reaction pathways. Process predictions were compared with both literature values and laboratory data. As a result of the development of this process simulation module, the chlorine dioxide substitution reaction may be linked to the rest of the bleaching sequence. Therefore, this important commercial practice may be evaluated through model studies.

Process Simulation of Chlorine Dioxide Substitution

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INTRODUCTION

Chlorine dioxide substitution for chlorine is being increasingly used in the chlorination stage of the kraft pulp bleaching sequence. This increased chlorine dioxide usage may be traced to modern environmental pressures to reduce the amount of chlorinated organics released into receiving waters from pulp mill bleaching effluents. Chlorine dioxide substitution has been experimentally shown to reduce the amount of absorbable organic halides (AOX) released into bleach plant effluent (Axegard, 1986).

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In addition to improving the environmental quality of bleaching liquors, chlorine dioxide substitution has also been found to affect the amount of lignin removal (Kappa number reduction) associated with the chlorination and first caustic extraction stages of the bleaching sequence (Rapson, 1958).

Almost all modern bleach plants use small amounts of chlorine dioxide as a replacement for chlorine in the chlorination stage. Typical addition levels range from 4-20% chlorine dioxide substitution on an active chlorine basis. The practice of chlorine dioxide substitution was started by Brown Company in Berlin, New Hampshire, during the early 1950s. Chlorine dioxide substitution was first used as a method of preventing strength loss due to higher reaction temperatures brought about by recycling. These recycling efforts were aimed at reducing the volume of wastewater that required treatment (Rapson and Anderson, 1958). Modern environmental concerns have increased the levels of chlorine dioxide substitution from the initial 4% to levels as high as 50-75%. Some mills even use 100% chlorine dioxide as a replacement for chlorine.

Despite the wide usage of chlorine dioxide substitution throughout the pulping industry, very little is known about the reaction pathways associated with chlorine dioxide substitution. Considerable amounts of data have been published detailing the macroscopic effects of chlorine dioxide substitution (Libergott et al., 1990). These papers indicate that the order of addition and the amount of chlorine dioxide substitution used produce vastly different physical results.

The current work models chlorine dioxide substitution over the complete range of process reaction conditions. The kinetics used to dictate the model performance assume, in simplest form, that chlorine-chlorine dioxide substitution reactions occur through a series of

competing/parallel reaction pathways (Hart and Hsieh, 1991). In order to use this reaction sequence, an understanding of pure chlorination kinetics and pure chlorine dioxide kinetics must be obtained. Also, the mechanism that was used to describe chlorine dioxide substitution must include provisions to explain the unique phenomena associated with the process.

The current model was used to perform a series of case studies covering the entire range of process operating conditions. These predictions were then compared to literature and experimental values to determine the effectiveness of the assumed kinetics and reaction pathways.

THEORY OF CHLORINE BLEACHING KINETICS

The fundamental purpose of bleaching is to brighten the pulp entering the bleaching sequence. Pulp brightness is strongly influenced by the specific light absorption coefficient of the fibers; as light absorption decreases, brightness increases. Most of the light absorbing bodies in fibers, the chromophoric functional groups, tend to be located in the amorphous or lignin fractions of the fiber matrix.

The basic effect of chlorine bleaching is to dissolve or modify these chromophores. The lack of selectivity of chlorine toward lignin results in a broad range of degradation reactions in which lignin is converted into multiple chlorinated and oxidized forms. At high reaction severity, chlorine may also attack crystalline elements, such as cellulose, in the fiber matrix. Cellulose degradation results in a direct loss of strength.

Extensive studies of chlorine and chlorine dioxide reactions with wood pulps have been conducted. The complex nature of the lignin

reactions with both chlorine and chlorine dioxide have resulted in the development of several reaction schemes. Furthermore, each bleaching chemical appears to be selective toward different fractions of the total lignin as shown in Figure 1. Lignin is assumed to consist of forms which are suspended in the liquid phase and those which are dissolved. Within each suspended and dissolved form are components which are highly reactive, moderately reactive, and inert to attack by bleaching chemicals such as chlorine and chlorine dioxide. Chlorine dioxide reacts with all suspended forms of lignin, whereas chlorine reacts most rapidly with fast lignin and less rapidly with slow lignin
regardless of physical form (i.e., suspended or dissolved).

To date, no comprehensive theory of chlorine dioxide substitution reaction involving both chlorine and chlorine dioxide has been developed. Kinetics developed by Germgard for prebleaching stages with chlorine dioxide and small amounts of chlorine did not indicate that parallel reactions were occurring. (Germgard, 1982). The theory presented here assumes that chlorine and chlorine dioxide compete for various lignin components (Jones, 1990). We further assume that the lumped-parameter kinetic models developed for chlorine alone and chlorine dioxide alone can be combined to represent the competitive/parallel reaction sequence (Jones, 1990). Laboratory evaluations have indicated that the above theory provides a simple description that reasonably approaches the chlorine dioxide substitution mechanism (Hart and Hsieh, 1991). Jones used this theory in the development of the MAPPS CSUBD simulation module.

C_D MODEL

The lumped-parameter kinetic models for chlorine and chlorine dioxide, used by Jones to construct the CSUBD simulation model, are outlined below

(Jones, 1990). As these are complex reaction sequences that involve multiple reaction products, pH changes and effects, fiber buffering capacity, carbohydrate shive reduction, and equilibrium conditions for multiple reacting species, the number of chemical and kinetic constraints that are involved in computing the kinetics becomes considerable. Numerical solution of these stiff ODE's results in another large system of equations. By overlaying the chlorine and chlorine dioxide kinetics, a system of well over 100 equations resulted. The entire set of equations has not been included in this paper due to the complexity of the reaction system. However, this complete system of equations is available from the Institute of Paper Science and Technology (Jones, 1990).

The actual kinetic parameters used in the operation of this model need to be altered as the amount of chlorine dioxide substitution is increased. A sharp transition in the rate of ClO_2 consumption has been found to exist (Germgard et al., 1982). As the level of substitution is increased, the preferential consumption of chlorine relative to chlorine dioxide changes. The location of this transition changes with the order of addition of Cl_2 and ClO_2. The order of addition will also affect the kinetic parameters in another manner. If chlorine is added before chlorine dioxide, the effectiveness of chlorine dioxide toward delignification is reduced because the ClO_2 acts as a free radical scavenger more rapidly than as a delignifying agent (Pryke, 1985). All of the simulation case studies that were conducted took these phenomena into account through the judicious selection of kinetic parameters.

The C_D reaction model assumes the reaction sequence occurs in a tower. A pulp stream is forced upward through the tower. Bleaching chemicals are injected and thoroughly mixed with the pulp at one to four

variable locations above the inlet. The time between each injection is determined by the placement of the injection point. The C_D tower model is based on the following assumptions:

1. Reactions of lignin with chlorine and chlorine dioxide are competitive but do not interact with each other (i.e., the rate equations do not contain interactive terms).
2. The competitive reaction scheme is described by the equations listed below, and the assumptions involved in each scheme apply to the combined system.
3. The tower behaves as a plug flow reactor with perfect radial mixing and zero back mixing of components.
4. The tower is adiabatic and assumed to be isothermal between injection points.

Chlorination Kinetics (Ackert et al., 1975)

Chlorine reacts with lignin to produce a suspended chlorolignin and HCl. Chlorination takes place through two simultaneous and parallel first order reactions:

$$L_f + a\ Cl_2 \rightarrow b\ L_fCl + c\ HCl \qquad (1)$$

$$L_s + a\ Cl_2 \rightarrow b\ L_sCl + c\ HCl \qquad (2)$$

where L_f and L_s are fast and slow portions of the total lignin, and L_fCl and L_sCl are the chlorinated products produced. XL_f and XL_s are the weight fraction of fast and slow lignin, respectively, relative to total suspended organics, POD:

$$XL_f = X_f\ TL \tag{3}$$

$$XL_s = X_s\ TL \tag{4}$$

where TL is the relative amount of suspended and dissolved lignin, and the amount subject to chlorine attack given by

$$TL = \frac{F_{sl} + F_{dl}}{POD} \tag{5}$$

POD is the total amount of suspended and dissolved organic pulp components,

$$POD = F_c + F_{sl} + F_{sh} \tag{6}$$

and X_f and X_s are the fractions of fast and slow lignins in the total reactive lignin. Fast and slow lignin encompass both suspended and dissolved forms. Both fast and slow lignin are assumed to have the same

stoichiometric constants, a, b, and c. The rate equations are also identical in form. They are assumed to be first-order ordinary differential equations. The rate constant for each of these equations is assumed to be of the standard Arrhenius form with activation energy, ΔE_c, and pre-exponential factor, A_j. The fast and slow reactions combine to yield an algebraic relationship for fast lignin in terms of slow reacting lignin:

$$\frac{X_f}{X_{fi}}^{k_s} = \frac{X_s}{X_{si}}^{k_f} \tag{7}$$

The slow lignin reaction rate defines the overall rate of chlorine reaction.

$$\frac{dX_s}{dt} = -k_s X_s Cl \tag{8}$$

Chlorine Consumption

The change in chlorine consumption, ΔCl, is based on the relative change in fast and slow lignin:

$$\Delta Cl = K_0 \, (\Delta XL_f + \Delta XL_s) \, \frac{POD}{F_w} \tag{9}$$

Chlorine Dioxide Kinetics (Teder and Tormund, 1980)

Chlorine dioxide reacts with suspended lignin in solution to form an oxidized lignin, acid, and various degradation products such as chlorite and chlorate ions:

$$L_{sl} + a\ ClO_2 + H_2O \rightarrow b\ L_{sl}OX + c\ H^+ + c\ ClO_2^- + d\ ClO_3^- \tag{10}$$

In the original Teder and Tormund model, lignin concentration was expressed in terms of the light absorption coefficient of the pulp, CK, which is found to be directly proportional to lignin content. The rate of disappearance of suspended lignin is a function of XL_{sl},

$$\frac{dXL_{sl}}{dt} = -k_0\ XL_{sl}^3\ CD^{0.5}\ H^{+(-0.3)} \tag{11}$$

The highly nonlinear form of the rate equation indicates that the effective rate is probably not intrinsic but rather mass transfer limited. The rate constant, k_0, depends on the initial lignin concentration and temperature.

$$k_0 = K_1 \left(\frac{K_2 + 1}{(XL_{sl}^i + 0.012)^2} \right) e^{\frac{-\Delta E_{cd}}{RT_{abs}}} \tag{12}$$

CXL_{sl} is the fraction of suspended lignin defined as (RL)(TL) where RL is the ratio of suspended to total lignin. Note that TL is defined relative to total suspended organics, POD. The weight fraction of suspended lignin for chlorine dioxide attack, XL_{sl}, is defined as

$$XL_{sl} = \frac{F_{sl}}{F_{sl} + F_{dl}} \tag{13}$$

Chlorine dioxide consumption depends on the bleaching sequence and the overall change in lignin concentration.

$$CD = CD^{i} - K_3 \ln\left(\frac{XL_{sl}^{i} + 0.012}{XL_{sl}^{n} + 0.012}\right) \tag{14}$$

The constant 0.012 results from the linear relationship between the lignin content and the light absorption coefficient given by

$$C_{\infty} = 0.012 = \frac{CK_c}{CK_1 - CK_c} \tag{15}$$

One of the problems associated with using ClO_2 is the degradation of the main reactant to nonreactive forms, such as chlorite, ClO_2^-, and chlorate, ClO_3^- ions. The equilibrium concentrations of these degradation products depend on the local pH (Rapson and Anderson, 1977).

pH > 3

$$ClO_2^- = CD\ (K_5 + K_6\ pH + K_7\ pH^2) \tag{16}$$

pH ≤ 3

$$ClO_3^- = CD\ (K_8 + K_9\ pH + K_{10}\ pH^2) \tag{17}$$

Acid-Base Equilibrium

Acid-base equilibrium is complicated by the presence of pulp fibers which interact physically and chemically with the pulp components in the homogeneous phase leading to ion exchange and swelling of the fibers. These interactions result in a significant buffering capacity of the fiber. When modeling acid-base equilibrium, the reaction scheme examines the H^+ ions produced by ClO_2 consumption, the change in OH^- concentration, and the moles of water produced by neutralization reactions.

Overall Mass Balances

The mass flows of each of the products and reactants are defined at any point in the tower by the following stoichiometric relations (current values are assumed):

$$F_{cd} = 0.067453\ CD\ F_w \tag{18}$$

$$F_{cl} = Cl\ F_w \tag{19}$$

The change in chlorate flow is determined by

$$\Delta F_{clo3^-} = (K_8 + K_9\ pH + K_{10}\ pH^2)\ \Delta F_{cd} \tag{20}$$

The change in chlorite flow is as follows:

$$\Delta F_{clo2^-} = (K_5 + K_6\ pH + K_7\ pH^2)\ \Delta F_{cd} \tag{21}$$

Additional materials are subjected to mass balance and control. A partial list includes the conversion of shives to the carbohydrate portion of the entering slurry and an overall balance on the ionizable species that enter and leave the tower. Water, hydronium ion, and hydroxide ion are also balanced throughout the reaction tower.

A considerable amount of attention has been devoted to the modeling of the conversion of lignin from the dissolved and suspended forms into chlorinated and oxidized lignin forms. The kappa number, a quantitative, industrially used measurement of the extent of bleaching, is directly proportional to the current weight fraction of suspended lignin:

$$\mathbf{K} = 660 \frac{F_{sl}}{POD} = 660\ XL_{sl} \tag{22}$$

The lignin conversion by chlorine reaction is defined as

$$CONV_1 = \frac{XL_f^i - XL_f + XL_s^i - XL_s}{XL_f^i + XL_s^i} \tag{23}$$

Chlorine conversion relative to the change in kappa number is based on the summation over all inlets and injection points.

$$C_{cl} = 100 \frac{\sum F_{cl}^i - \sum F_{cl}^n}{POD\ (\mathbf{K}^i - \mathbf{K}^n)} \tag{24}$$

Lignin conversion, CONV, is defined as the change in suspended lignin relative to entering suspended lignin. The conversion of entering dissolved lignin is not included in this definition.

$$CONV = 100 \frac{1 - XL_{sl}}{XL_{sl}^i} \tag{25}$$

Overall mass balance calculations are updated at each injection point. No reactions are assumed to take place at the injection points.

$$F = \sum_{j=1}^{n} F_j^e \tag{26}$$

where e refers to all components entering the injection point and F is mass flowrate. The slurry density is also updated after each injection based on the new composition.

Energy Balance

The enthalpy of the pulp slurry at a given point in the tower, H, is defined in terms of the sum of the enthalpy of formation, H_{fm}, and the integrated heat capacity from the reference temperature, T_r, to the current temperature, T, over the components.

$$H = \sum_{j=1}^{n} \left(H_{fmj} + \int_{T_r}^{T} Cp_j \, dT\right) F_j \tag{27}$$

where j refers to the component. Based on the assumption that the bleaching tower behaves in an adiabatic manner and is isothermal between injection points, the slurry temperature is initialized at the entrance and recalculated only at the injection points and the reactor exit (i.e., the top of the tower). The cup-mixed temperature, T, is calculated at each injection and mixing point by

$$T = \sum_{n=1}^{2} \frac{H_n}{F\ Cp_a} \tag{28}$$

where Cp_a is the weighted average specific enthalpy, and n refers to the nth stream.

NUMERICAL TECHNIQUE

Bleaching reactions are characterized by a rapid initial phase followed by a very slow final phase. Conventional approaches require extremely small time steps and repeated integration in order to integrate over the slow final phase. A more efficient approach was needed. The new semi-implicit approach, developed by G.L. Jones, reverses the roles of the independent and dependent variables and is referred to as the reverse-variable approach (Jones, 1990). The reversal of variables also serves to improve the accuracy of the solution. In the present scheme, the two dependent variables, slow lignin fraction, X_s, and suspended lignin fraction, XL_{sl}, are manipulated, and the time step required for the limiting reaction is determined. All other results such as chemical consumptions and other stoichiometric reactions are derived once the limiting rate is determined.

Given the two trial increments in reactive lignins, the consumption of bleaching chemicals is determined from the stoichiometric relations. The effective rate constants are determined from the stoichiometric relations. The effective rate constants are determined based on lumping the average concentrations of all components other than the reacting lignins into the reaction rate constants. The reaction kinetics are then integrated semianalytically over the reaction time increment, one for each reacting lignin. Since the bleaching chemicals are competing for

essentially the same reactive lignin components, the faster reaction will have the shorter reaction time step. The actual time increment is set to the smaller of the two time increments, and the actual increments in reactive lignins, DDL and DXS, are rescaled based on the ratio of the time increments. One of the two reactions predominates, and the trial increment for the predominant reaction is not rescaled during that time step.

The concentrations are updated with the new trial increments, and the chemical consumptions are recomputed. Checks are made for limiting concentrations and time. Special cases, such as imminent consumption of chlorine, ClO_2, or the violation of the time constraint, result in a special computation and re-evaluation of the time increments.

Checks are made at each step to determine if limiting conditions have been met. Limiting conditions are consumption of reactants, i.e., lignins, bleaching chemicals, or reaction time exceeding reactor space time.

The initial trial increment for ClO_2 reactive lignin, ΔXL_{s1}^{t}, and slow chlorine reactive lignin fraction, ΔX_s^{t}, are assigned values based on the initial concentrations of each component.

$$\Delta XL_{s1}^{t} = \frac{XL_{s1}^{i}}{ML} \tag{29}$$

$$\Delta XL_s^t = \frac{XL_s^i}{ML} \tag{30}$$

where ML, the maximum number of increments, is generally greater than 10.

Integration Procedure

New values of X_s, X_s^n and X_f, X_f^n are defined as follows:

Chlorination Reactions:

If CL > 0.0, the slow lignin fraction is decremented by the trial increment, ΔX_s^t

$$X_s^n = X_s^0 - \Delta X_s^t \tag{31}$$

$$XL_s^n = X_s^n \, TL^n \tag{32}$$

If the trial increment is larger than the remaining slow lignin, the increment is set to X_s^0, and the new trial value of X_s, X_s^n, is set to zero. If the chlorine concentration is currently zero, all chlorination reactions cease, and the fast and slow lignin fractions remain unchanged. The current concentration of fast lignin is determined directly from Equation 7.

$$X_f^n = X_s^{n\,(k_f/k_s)}$$

(33)

If X_s^n is zero, X_f^n is based on the average value of X_s over the increment,

$$X_f^n = \left(\frac{X_s + X_s^n}{2}\right)^{(k_f/k_s)}$$

(34)

The change in X_f is given by

$$\Delta X_f^t = X_f - X_f^n$$

(35)

If the predicted change in chlorine exceeds the current chlorine concentration, the new chlorine concentration, Cl^n, is obtained directly by decrementing Cl with ΔCl, and the average chlorine concentration is defined as

$$Cl^a = \frac{Cl^0 + Cl^n}{2}$$

(36)

The trial time increment to consume the specified fraction of slow lignin is determined by pseudoanalytic integration of Equation 8.

$$\Delta t_{cl} = -\ln\left(\frac{\frac{X_s^n}{X_s^0}}{K_{22}\ Cl^a}\right) \tag{37}$$

where

$$K_{22} = 3600\ K_1\ e^{\left(\frac{\Delta E_{cl}}{RT}\right)}\ \frac{\rho}{(k_f/k_s)} \tag{38}$$

ρ is the local slurry density and the ratio k_f/k_s is assumed to be so for this work.

$$K_0 = K_{D1}\left(K_{D2} + \frac{1}{(DL^0 + C_w)^2}\right) e^{\left(\frac{\Delta E_{cd}}{RT}\right)} \tag{39}$$

If the reaction conditions are not met, Δt_c is set to zero.

The test for reaction with ClO_2 requires the concentrations of suspended lignin, XL_{s1}, chlorine dioxide, and hydronium ion all be positive. If this test is met, the suspended lignin concentration, DL, is incremented by the trial value ΔDL^t to give the new trial value $XL_{s1}{}^t$. If $\Delta XL_{s1}{}^t > XL_{s1}{}^0$, the remaining lignin, it is assumed that no further chlorine dioxide reactions occur, and the actual increment is $XL_{s1}{}^0$. In

this case, the new value of XL_{s1}^{n} is determined directly from the kinetics,

$$XL_{s1}^{n} = \frac{XL_{s1}^{0}}{(1 + (XL_{s1}^{0})^2 \, KB \, \Delta t_{cd})^{0.5}} \tag{40}$$

The chlorine dioxide consumption is given by the following algorithm:

$$\Delta CD = K_3 \ln\left(\frac{C_\infty + X_{s1}^{0}}{C_\infty + X_{s1}^{n}}\right) \tag{41}$$

If the predicted increment in CD exceeds the current concentrations, the increment is reset to the current value, and the new value is set to zero. The average concentration is based on the new and old values. The trial time step for ClO_2 reaction is given by

$$\Delta t_{cd} = \frac{\left(\frac{1}{(XL_{s1}^{n})^2} - \frac{1}{(XL_{s1}^{0})^2}\right)}{KB} \tag{42}$$

where

$$KB = 2\ K_0\ \frac{CD^{0.5}}{H^{0.3}} \tag{43}$$

At the last time step, when XL_{sl}^{n} becomes zero, Δt_{cd} is based on the average value of XL_{sl} over the increment,

$$\Delta t_{cd} = \frac{\left(\frac{1}{(XL_{sl}^{a})^2} - \frac{1}{(XL_{sl}^{0})^2}\right)}{KB} \tag{44}$$

As with chlorination, if the reaction conditions are not met, the lignin concentration is not changed, and Δt_{cd} is set to zero.

Determining The Limiting Reaction Rate

The limiting reaction rate is defined as the minimum of Δt_{cl} and Δt_{cd} provided they are both positive. Otherwise, Δt is set equal to whichever variable is positive. If neither Δt_{cl} nor Δt_{cd} is positive, no reactions take place within this increment.

Rescaling of Increments

The changes in XL_s and XL_{sl} are rescaled based on the ratio of the minimum constrained time step and the trial time step for each reaction, provided each is nonzero. Otherwise, no rescaling takes place.

$$XL_s^n = XL_s^n \frac{\Delta t}{\Delta t_{cl}} \tag{45}$$

$$XL_{sl}^n = XL_{sl}^n \frac{\Delta t}{\Delta t_{cd}} \tag{46}$$

The rescaling enforces the changes which must occur for two competing reactions. The faster of the two reactions will have the smaller time increment, and Δt will equal this smaller time step. The corresponding trial change in either XS or DL will not be rescaled. However, the slower of the two reactions depending on the reaction conditions, will be rescaled by the relative time steps.

Because of rescaling, it is necessary to recompute the new values of X_s^n and DL^n and to test for violation of concentration constraints, i.e., exhaustion of lignins. The same procedure is followed in determining fast lignin concentration from slow lignin and the consumption of chlorine and chlorine dioxide. Further checks are made to ensure that the concentration constraints on these chemicals are not violated.

Limiting Conditions

A variety of limiting conditions are handled by the algorithm. These conditions include $t_n > \tau$, exhaustion of chlorine or chlorine dioxide, or violation of the non-negativity constraint on the time steps. Each of these situations is handled differently. For example, if one or both time increments is zero, no reactions take place in this section of the reactor. However, this does not preclude that additional reactants

could not be introduced at some point farther on. In this case, the time increment is based on remaining space time divided by the remaining iterations. If $t^n > \tau$, the time constraint is violated and $t^n = \tau$ and $\Delta t = \tau - t^0$.

Injection Control

When the current position in the reactor, Z, exceeds one of the injection points, the current reactor components are mixed with the next injection stream. When injection occurs, the thermodynamics of the mixture are updated using the enthalpy balance and the cup mixed temperature. All pertinent component concentrations are reinitialized, and the total mass flow rate, slurry density, volumetric flow rate, space time, and linear velocity are reinitialized. Finally, all temperature dependent variables such as activation energy terms and rate constants are reinitialized.

PROCESS SIMULATION OF CHLORINE DIOXIDE SUBSTITUTION

Once the model and solution technique were developed, a series of process simulation predictions were obtained. These predictions were used to determine the effectiveness of the process model. The assumption that the reaction kinetics associated with chlorine dioxide substitution consisted of a competing/parallel reaction pathway would be considered adequate if reasonable agreement was obtained between the prediction and the experimental data (Hart and Hsieh, 1991). A simple simulation flow sheet was constructed to assist in this effort. The simulation study consisted of an entering thick stock, the chlorine-chlorine dioxide bleaching tower, a chlorination washer, heat exchanger for the stock entering the caustic extraction stage, and a caustic extraction tower. The MAPPS process flow sheet is shown in Figure 2. In order to ensure

all of the performance attributes and physical properties of the entering brownstock pulp were consistent with the MAPPS simulation program, a pre-existing MAPPS brownstock stream was used (Hart and Hsieh, 1990).

The simulation studies were divided into multiple parts. The first portion of the work examined the limiting cases where no chlorine or no chlorine dioxide was present for reaction. If either of these cases did not accurately predict experimental results, the resulting substitution studies would not be of any value. Errors in the limiting cases would mean that the original kinetics for the individual reactions were inaccurate. As long as the majority of the macroscopic properties predicted by the limiting case studies were observed in the model predictions, the overlaid kinetic scheme developed for chlorine dioxide substitution could be used for the remainder of this work. If the macroscopic properties were not in close agreement with the actual laboratory data, further modeling work would be required.

After the chlorine and chlorine dioxide kinetics were confirmed through the limiting studies, the predicted model effects of the order of addition of chlorine and chlorine dioxide were examined. Good agreement between the model predictions and experimental data would be used as a method to verify the theory that chlorine dioxide substitution was a simple case of competing/parallel reactions. It was assumed that if the competing/parallel kinetic model of chlorine dioxide substitution predicted similar results to actual macroscopic laboratory and literature data, the resulting kinetics could be successfully described by the assumed process.

Limiting Case Study 1 - 100% Chlorine

Two limiting case studies were conducted for 100% chlorine. These studies included a determination of the effects of chlorine concentration

and a reproduction of the kinetics of delignification at short reaction times. Laboratory data (Hart and Hsieh, 1991) indicate that the kappa number should rapidly decrease as the amount of applied chlorine is increased from 0 to about 6 wt% based on bone dry pulp. Above 6 wt% active chlorine, the kappa number versus applied chlorine curve should flatten out and approach a near steady value. The simulation predictions agreed quite well with the actual experimental data. A comparison of the predicted and experimental values is shown in Figure 3.

The predicted kinetics of delignification (kappa number reduction) at short reaction times were also compared to experimental data. The resulting comparison for short reaction times, shown in Figure 4, indicates the existing kinetic equations follow the trend of delignification at short times. However, the actual level of delignification is underpredicted. At long reaction times, 30 minutes or greater, excellent agreement between empirical data and predicted values was obtained (Figure 3). In order to accurately predict chlorination kinetics for short reaction times, the existing model must be modified.

Limiting Case Study 2 - 100% Chlorine Dioxide

Two different limiting case studies were examined for 100% ClO_2. The first case study was similar to the limiting case study used for chlorine. The second case study examined the effects of reaction time in the bleaching tower on the kappa number reduction. Fair agreement was obtained between the predicted and actual values of kappa number for the first limiting case study (see Figure 5). The results of the second limiting case study varied depending upon which time frame was examined. Figure 6 shows the effects of reaction time on the amount of delignification by 100% chlorine dioxide. For short time periods, less

than one minute, the model tended to underpredict the amount of delignification. At longer times, the model agreed fairly well with the empirical data.

The variations between the actual and predicted values tend to indicate the kinetic model for chlorine dioxide delignification does not completely describe the experimental data. Some subtle effects of chemical parameters like chloride ion concentration may be affecting the kinetic pathway of chlorine dioxide delignification. Despite the fact that the chlorine dioxide kinetics do not completely define the actual bleaching process, the predicted values of delignification seem to exhibit the majority of the macroscopic properties noted in chlorine dioxide delignifi-cation. For this reason, the chlorine dioxide model was not altered before attempting the ClO_2 substitution simulations.

Process Predictions - Chlorine Dioxide Substitution

The MAPPS flow sheet (Figure 2) used for the two limiting case studies was employed to study the effects of chlorine dioxide substitution. Substitution levels were varied from 0 to 100% chlorine dioxide. The amount of substitution was determined on an active chlorine basis. The chemical charge, on an active chlorine basis, was maintained at a constant level throughout the simulations. All experimental conditions are listed in Table 1 (Hart and Hsieh, 1991).

Two different sets of C_D simulations were conducted. The difference between the two sets was the order of chemical addition in the chlorination tower. One set of simulations injected chlorine into pulp as it entered the reaction tower. One minute later, chlorine dioxide was injected into the tower. Another set of simulations used chlorine dioxide as the entering chemical with a chlorine injection one minute

into the simulation. Two sets of experimental data were obtained using the process conditions listed above.

In order to account for the variation in preferential consumption of chlorine with respect to chlorine dioxide reported by Germgard et al., 1982, the kinetic parameters were varied during the process simulation studies. Only minor changes were made over the entire substitution range, in the kinetic parameters during each set of simulations. Only one kinetic parameter was altered for each of the changes. The kinetic parameters are listed in Table 2.

The only other change that was made in the kinetic parameters was associated with the order of addition. When chlorine is the initial chemical added to the pulp, free radicals form (Pryke, 1985). Chlorine dioxide acts as a rapid free radical scavenger when added after chlorine. To account for this deactivation of chlorine dioxide by chlorine free radical scavenging, one kinetic reaction parameter, XKD2, was altered.

A plot of the kappa number as a function of the percent chlorine dioxide substitution is shown in Figure 7. Two different sets of curves are shown in the figure. The top data set represents chlorine addition with a later chlorine dioxide injection. The bottom data set was obtained from chlorine dioxide addition first with chlorine injected at a later time. The lines in Figure 7 represent the model predictions, while the data points represent actual laboratory values. Reasonable agreement was obtained between the predicted and empirical data.

CONCLUSIONS

The reasonable agreement between the predicted values and laboratory data for C_D substitution indicates that the assumption of a competing/parallel reaction pathway has some validity. In order to

further verify this assumption, the chlorine dioxide portion of the kinetics should be modified to obtain better agreement with empirical data at long reaction times. Also, the early phase kinetics of both chlorine and chlorine dioxide need to be modified. Over the substitution range of 0 to 100% chlorine dioxide substitution for chlorine, minor changes in the rate variables were required for each of the C_D order of addition reaction sequences studied. The ultimate effect of these rate changes was an increase in the reaction rate of chlorine dioxide. If these rate changes were not made, the current model would have underpredicted the chlorine dioxide reaction rate at short reaction times.

The current simulation model contained in the MAPPS CSUBD module may be used to obtain reasonable macroscopic predictions of the C_D process. These macroscopic predictions include but are not limited to material and energy flows, pulp yield and kappa number and chemical consumption. The resulting process simulation may be used to evaluate the effects of various bleaching sequences and pulp prebleaching on the chlorination stage. However, care must be taken to ensure that proper reaction parameters for chlorine dioxide are used in the process simulation.

NOMENCLATURE

A	pre-exponential factor
AF	flow area
CD	chlorine dioxide concentration (molar)
CK	specific light adsorption coefficient
Cl	chlorine concentration (molar)
CLO2	chlorite ion concentration
CLO3	chlorate ion concentration

CONV	lignin conversion relative to change in kappa number
f	fraction of fast or slow lignin
F	mass flow rate
H	hydronium ion concentration (molar)
	enthalpy
k	rate constant
K	stoichiometric constant
KAPPA	kappa number (lignin content)
L	lignin component
ML	maximum number of increments
OH	hydroxide ion concentration (molar)
pH	pH
POD	total suspended organics
R	ideal gas constant
RL	ratio of suspended to total lignin
t	time
T	temperature
v	slurry linear velocity
V	reaction tower volume
W	water concentration (molar)
X	mass fraction
XKD	chlorine dioxide kinetic rate constant
XL	lignin content (mass fraction)
Z	axial distance

Greek Letters

Δ	increment
ρ	local slurry density
τ	space time

Subscripts

a	acid
abs	absolute
b	base
bcl	bound chloride
c	carbohydrate
cd	chlorine dioxide
cl	chloride ion
clg	chlorolignin
dc	dissolved carbohydrate
dl	dissolved lignin
f	fast lignin
h	hydronium ion
l	total lignin
oh	hydroxide ion
s	slow lignin
sh	shives
sl	suspended lignin
t	total
u	unreactive lignin
w	water

Superscripts

a	average value
i	initial value
n	current tower location
o	previous tower location

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Table 1. Experimental Bleaching Conditions.

Chlorination Stage:

Active Chlorine -	6.2018 wt% on bone dry pulp
ClO_2 Substitution -	0 - 100% ClO_2 based on active Cl_2
Consistency -	3.5 wt% pulp
Reaction Temperature -	30° C
Reaction Time -	30 minutes
Wash Water -	2.000 Liters

Caustic Extraction Stage:

NaOH -	3.5 wt% on bone dry pulp
Oxygen -	20 psig
Consistency -	10 wt% pulp
Reaction Temperature -	70° C
Reaction Time -	90 minutes
Wash Water -	2.000 Liters

Table 2. MAPPS Kinetic Parameters for CSUBD Module.

	Chlorine Added First		ClO_2 Added First	
Kinetic Parameter	Applicable Range	Value	Applicable Range	Value
*Actden	0-100%	-25368	0-100%	-25368
XKD1	0-100%	$2.6X10^{10}$	0-100%	$2.6X10^{10}$
XKD2	0-60%	1.0	0-40%	1.0
	70-100%	2.5	50-100%	5.0
XK3	0-100%	.001	0-40%	.001
			50-100%	.0005
XK4	0-100%	.7	0-100%	.7

*Actden = activation energy for chlorination reactions

XKD1 = rate constant for chlorine dioxide reactions

XKD2 = rate constant for chlorine dioxide reactions

XK3 = stoichiometric constant for chlorine dioxide

XK4 = stoichiometric constant for H^+ ion

Figure 1. Physical and Chemical Distribution of Lignin.

Figure 2. MAPPS Process Flow Sheet.

Figure 3. A Comparison Between Predicted and Laboratory Values. Kappa Number as a Function of Chlorine Charge - 100% Chlorine.

Figure 4. A Comparison Between Predicted and Laboratory Values. Kappa Number Reduction as a Function of Short Reaction Times - 100% Chlorine.

Figure 5. A Comparison Between Predicted and Laboratory Values. Kappa Number as a Function of Chlorine Dioxide Charge - 100% ClO_2.

Figure 6. A Comparison Between Predicted and Laboratory Values. Kappa Number Reduction as a Function of Short Reaction Times - 100% Chlorine Dioxide.

Figure 7. Order of Addition Effects on the Kappa Number at Various Levels of Chlorine Dioxide Substitution. Solid Line Represents CSUBD Model Predictions for Cl_2 Addition Followed by ClO_2. Dotted Line Represents CSUBD Model Predictions For ClO_2 Addition Followed by Cl_2.

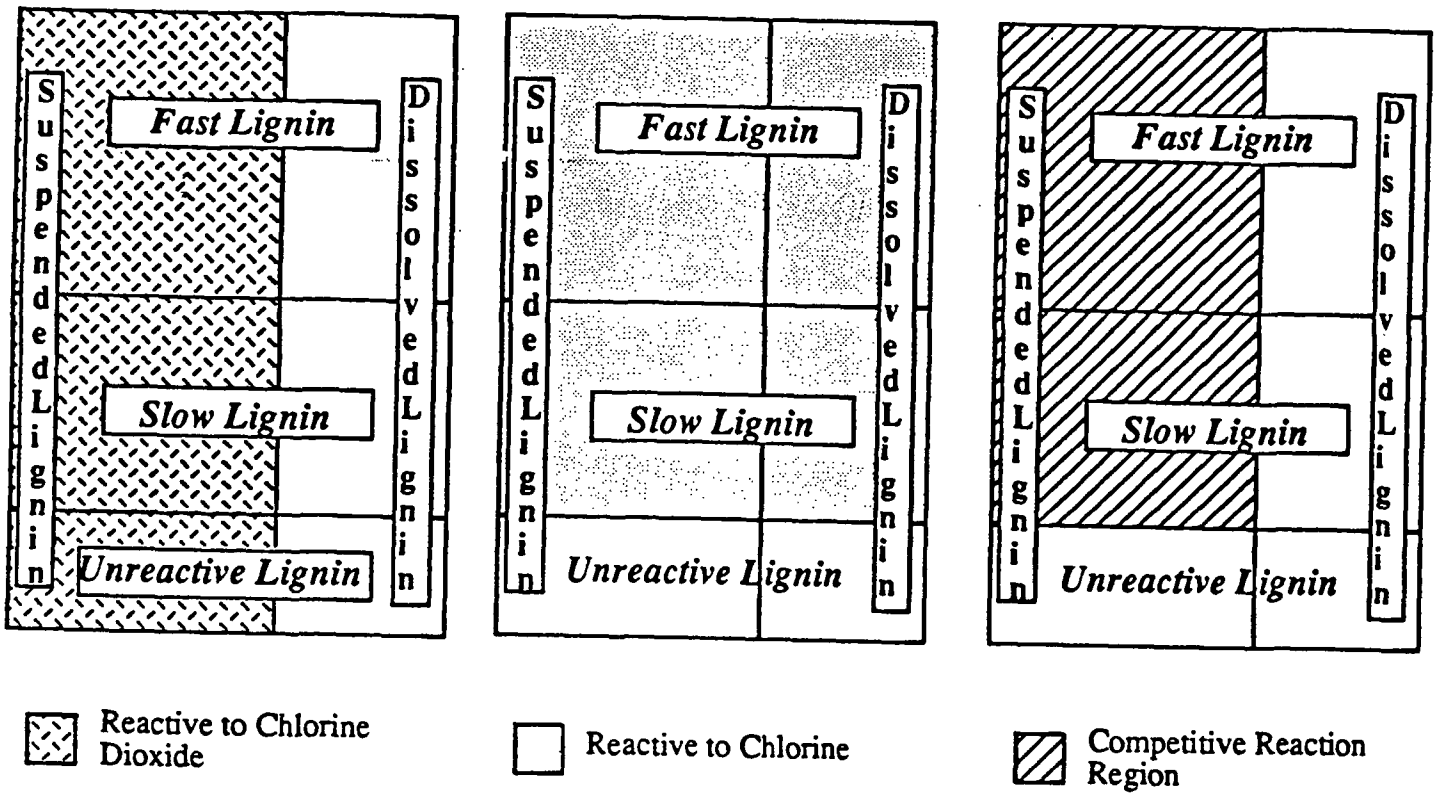


Figure 1. Physical and Chemical Distribution of Lignin

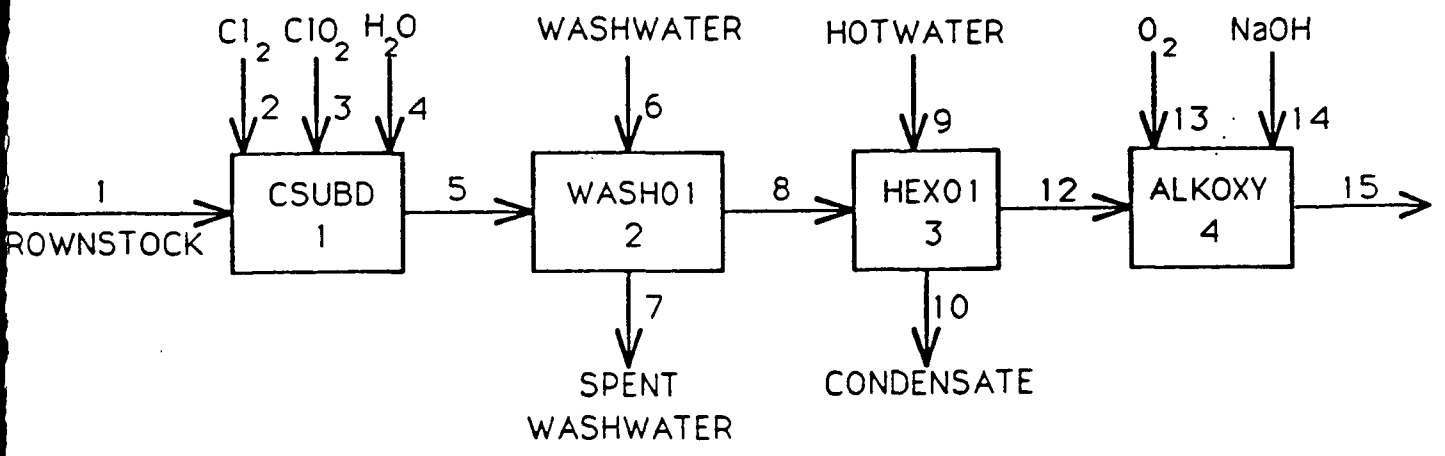


Figure 2. MAPPS Process Flowsheet.

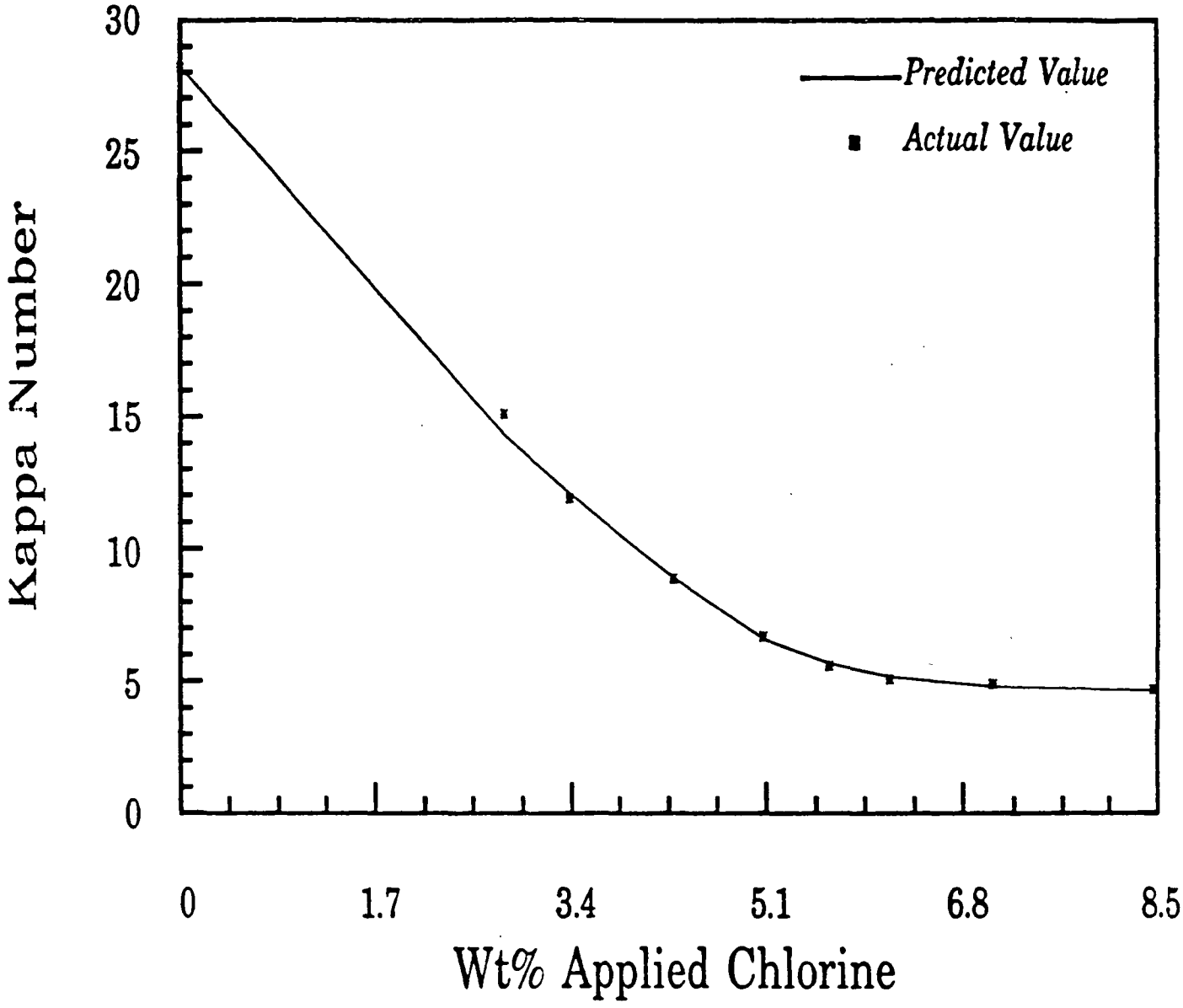


Figure 3. A Comparison Between Predicted and Laboratory Values. Kappa Number as a Function of Chlorine Charge - 100% Chlorine.

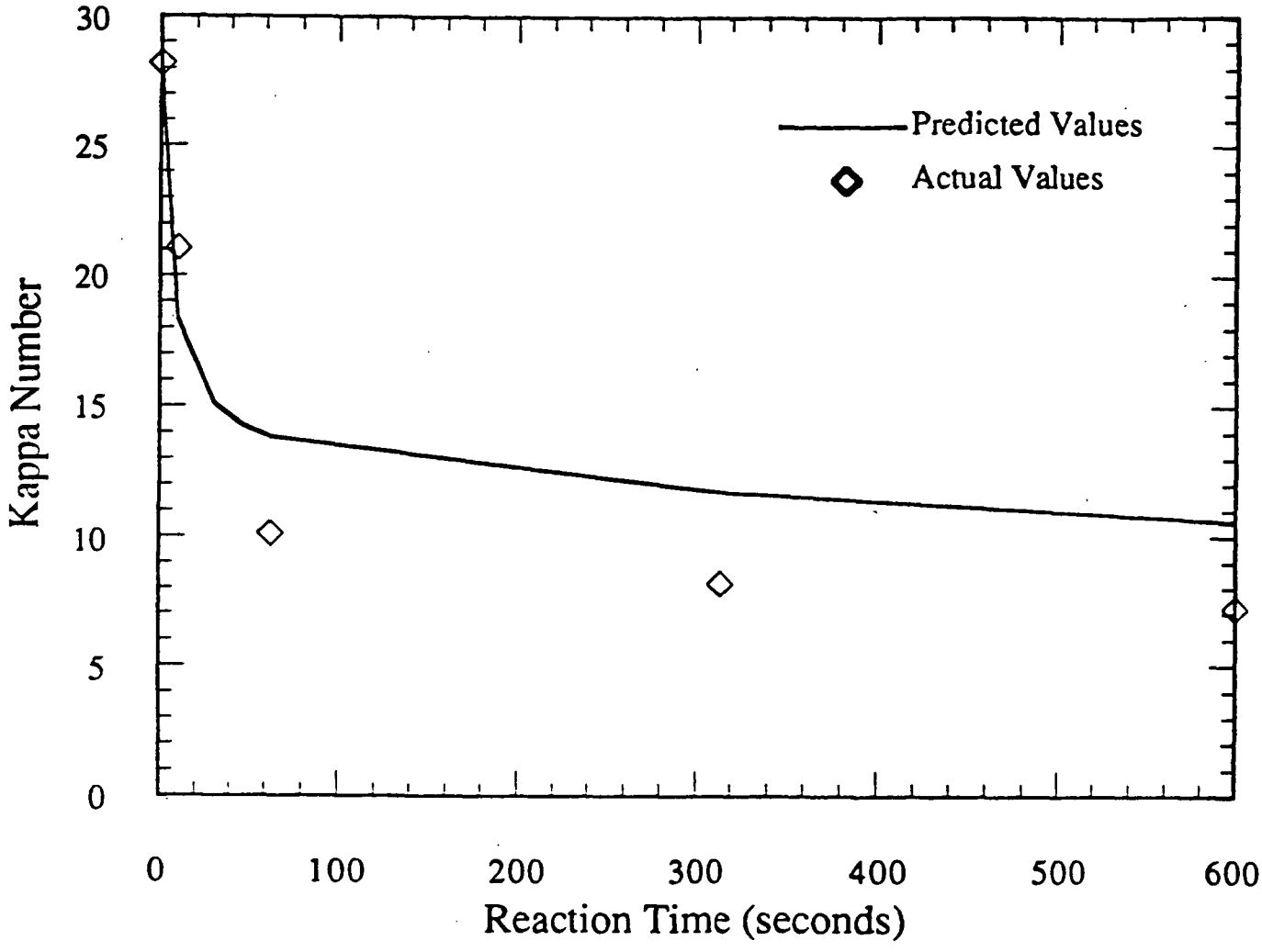


Figure 4. A Comparison Between Predicted and Laboratory Values. Kappa Number Reduction as a Function of Short Reaction Times - 100% Chlorine.

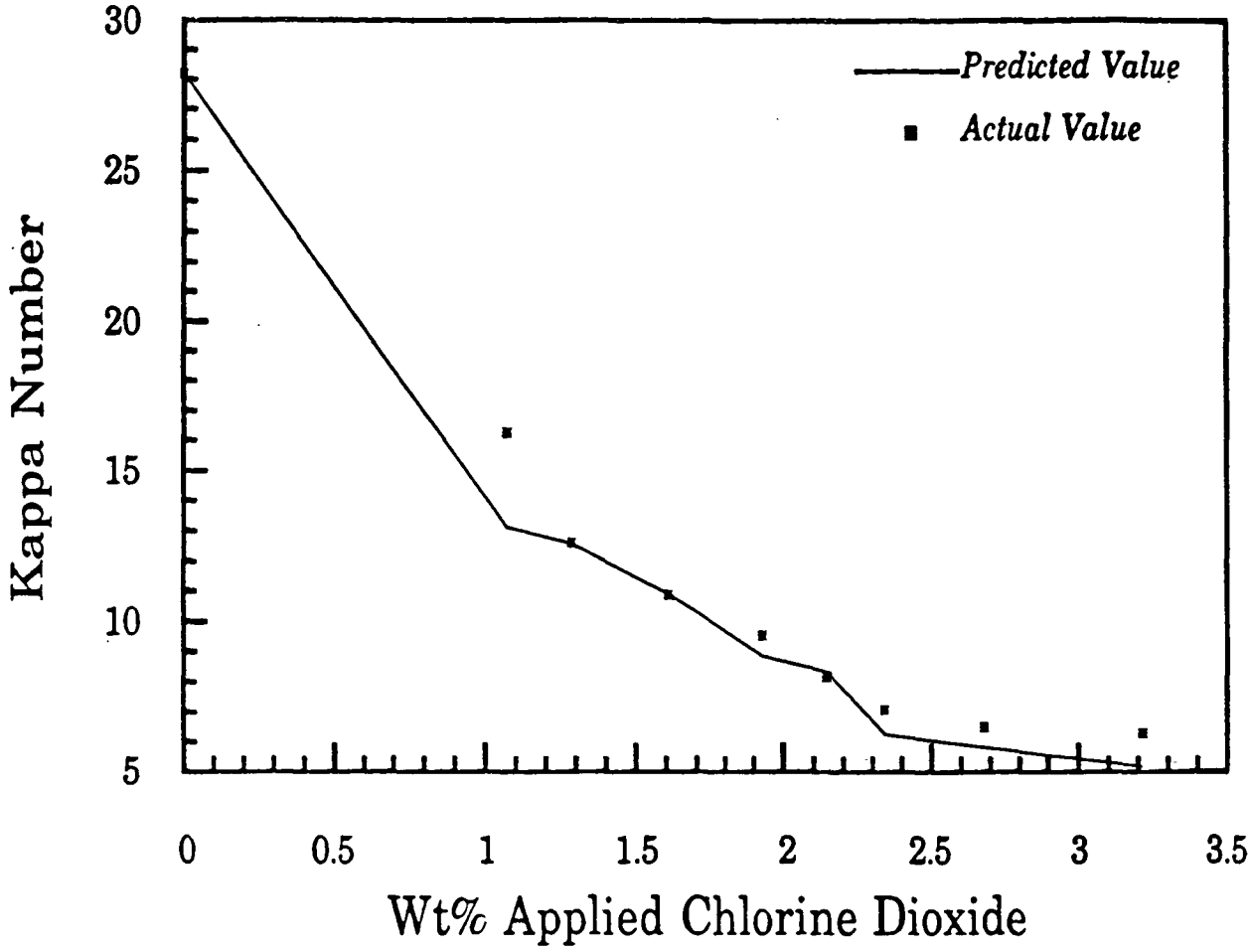


Figure 5. A Comparison Between Predicted and Laboratory Values. Kappa Number as a Function of Chlorine Dioxide Charge - 100% ClO_2

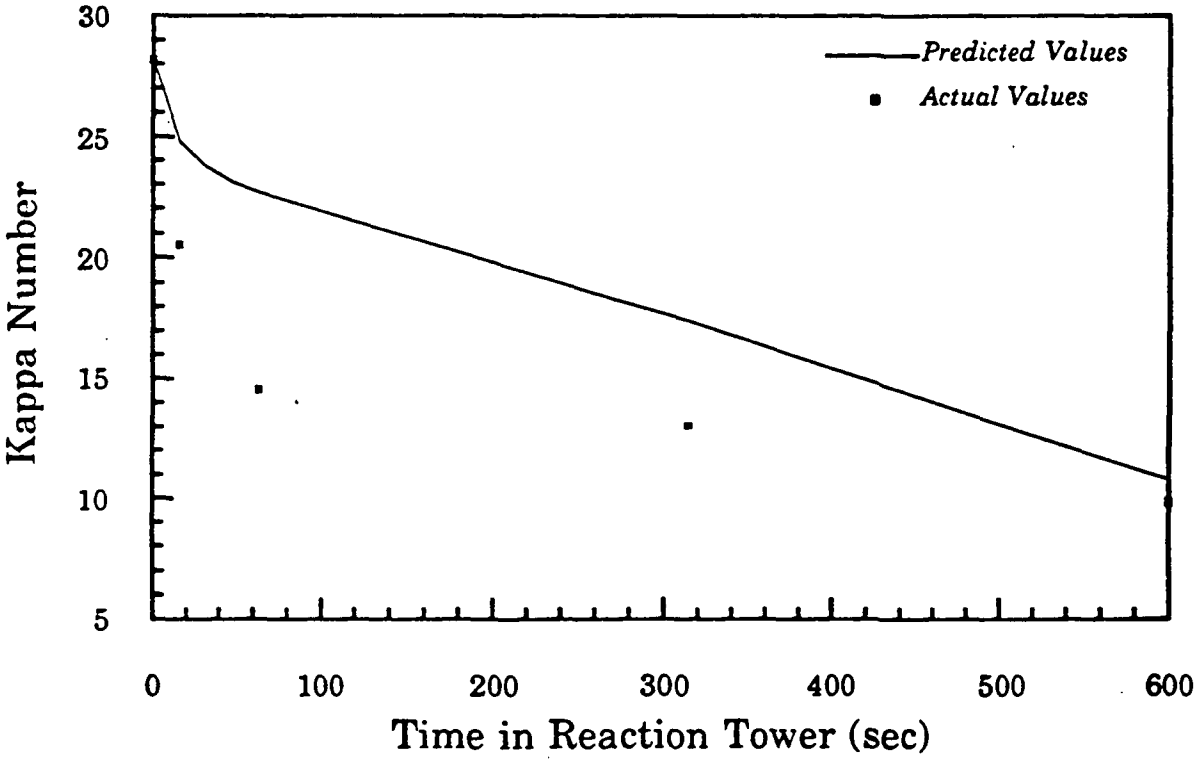
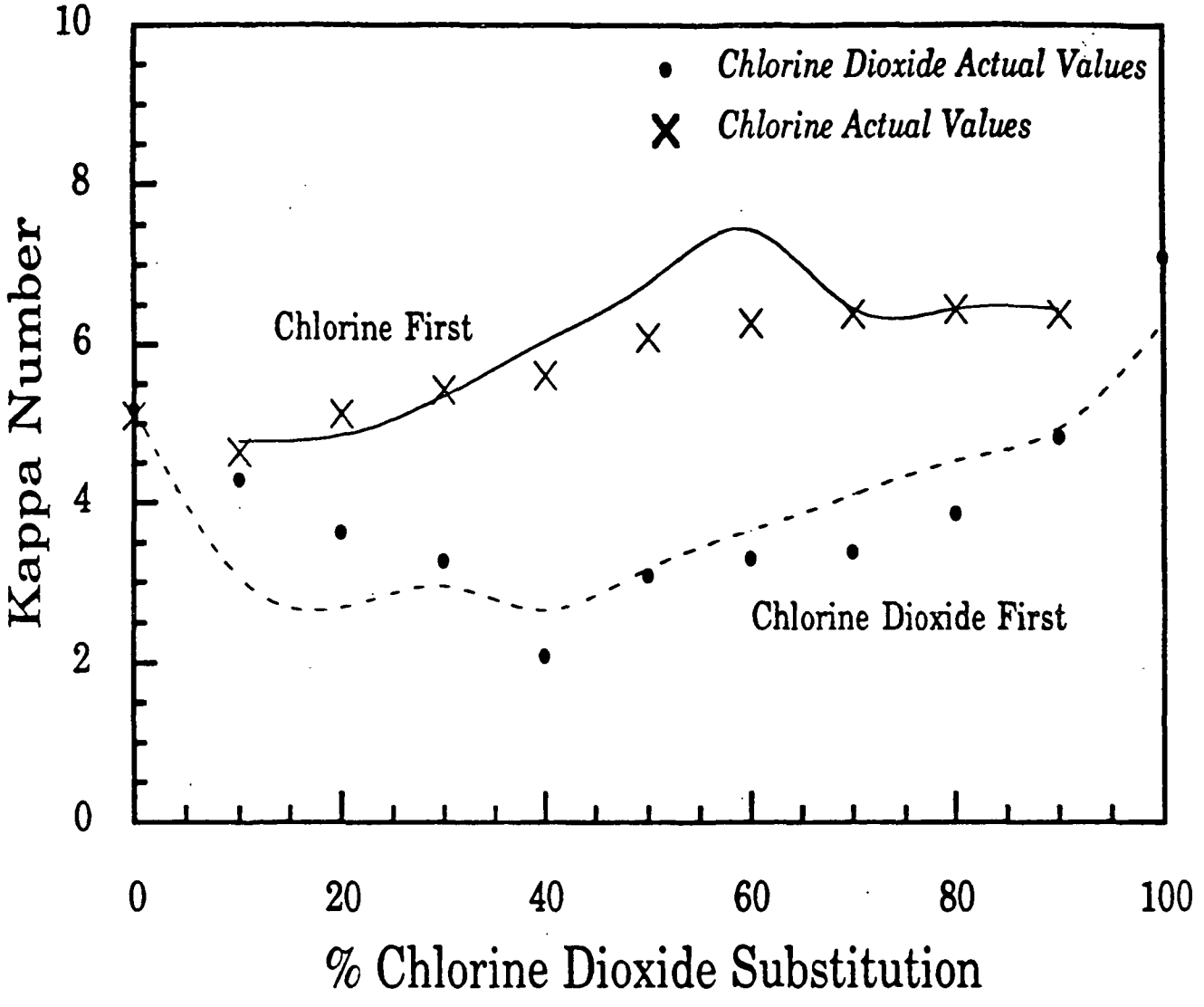


Figure 6. A Comparison Between Predicted and Laboratory Values. Kappa Number Reduction as a Function of Short Reaction Times - 100% Chlorine Dioxide.



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